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Revolutionary Systems for Catalytic Combustion and Diesel Catalytic Particulate Traps

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Revolutionary Systems for Catalytic Combustion and Diesel Catalytic Particulate Traps

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Abstract

This report is a summary of an LDRD project completed for the development of materials and structures conducive to advancing the state of the art for catalyst supports and diesel particulate traps. An ancillary development for bio-medical bone scaffolding was also realized.

Traditionally, a low-pressure drop catalyst support, such as a ceramic honeycomb monolith, is used for catalytic reactions that require high flow rates of gases at high-temperatures. A drawback to the traditional honeycomb monoliths under these operating conditions is poor mass transfer to the catalyst surface in the straight-through channels. "Robocasting" is a unique process developed at Sandia National Laboratories that can be used to manufacture ceramic monoliths with alternative 3-dimensional geometries, providing tortuous pathways to increase mass transfer while maintaining low-pressure drops. These alternative 3-dimensional geometries may also provide a foundation for the development of self-regenerating supports capable of trapping and combusting soot particles from a diesel engine exhaust stream.

This report describes the structures developed and characterizes the improved catalytic performance that can result. The results show that, relative to honeycomb monolith supports, considerable improvement in mass transfer efficiency is observed for robocast samples synthesized using an FCC-like geometry of alternating rods. Also, there is clearly a trade-off between enhanced mass transfer and increased pressure drop, which can be optimized depending on the particular demands of a given application. Practical applications include the combustion of natural gas for power generation, production of syngas, and hydrogen reforming reactions.

The robocast lattice structures also show practicality for diesel particulate trapping. Preliminary results for trapping efficiency are reported as well as the development of electrically resistive lattices that can regenerate the structure by combusting the trapped soot.

During this project an ancillary bio-medical application was discovered for lattices of hydroxyapatite. These structures show promise as bone scaffolds for the reparation of damaged bone. A case study depicting the manufacture of a customized device that fits into a damaged mandible is described.

Acknowledgements

The authors would like to thank Lindsey Evans and Ronald Sandoval for their general help and guidance with the flow reactor system and chemical synthesis procedures, and Paul Dailey for performing the pressure drop measurements. The bone scaffolding collaboration required invaluable contributions from Jennifer Dellinger, Russ Jamison, Michael Goldwasser, Ben Grosser, and Janet Hanlon from the University of Illinois and Dave Gill and Michael Savedra from Sandia National Laboratories. Special thanks are also extended to Dr. James E. Smay currently in the Chemical Engineering Department at Oklahoma State University for the creation and modifications of the robocasting software, and to Jill Rockwood and Mike Readey at Caterpillar Inc. for suggesting the catalyst and providing material references. This work was supported through Sandia's laboratory directed research and development (LDRD) program.

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1. Introduction

1.1 Technical Problem

Diesel particulate emission (soot) is becoming a global problem, and current technologies can not meet the regulations projected for 2007 in the U.S. Likewise, NOx formation from methane combustion in gas-turbine electric power plants is becoming a significant environmental concern. Uniting these two technical problems is the fact that they can both be addressed through the use of state-of-the-art, in-line ceramic filters/supports providing an appropriate catalytic function. However, these are extremely demanding applications. An in-line catalyst support or filter in a high velocity, high temperature, and corrosive gaseous stream must meet the following criteria for successful performance:1) a large surface area to volume ratio; 2) a high permeability for low pressure drop; 3) high strength and/or low thermal expansion; 4) high temperature corrosion resistance; 5) high trapping efficiency (for filters). Similarly, the catalyst must be very active, but thermally and chemically stable over a broad range of thermal and chemical conditions.

Joining all of these attributes in one package is extremely challenging, and even the best commercial attempts have fallen short. Johnson Matthey Inc has developed a two-stage diesel particulate trap that uses a primary converter to produce excess NO_2 and a secondary trap to capture and "burn" the soot, using the NO_2 as the oxidant. However, European tests have shown that this elaborate system is only marginally successful. Under perfect conditions (fuel with < 15 ppm sulfur, and engines that do not burn oil or lubricant), the traps are reported to function for 50,000 miles. In reality, impurities from fuel and engine oil induce rapid corrosion of the cordierite trap. Failure within 1 or 2 months is not uncommon. [1] Manufacturers of large diesel engines, who must eventually warranty these filter systems, have expressed concern regarding the suitability of cordierite. Also, the need to balance NOx and particulate formation for proper performance is not a very satisfactory approach. A catalytic system that directly utilizes air/oxygen for soot combustion, is not deactivated by components of the particulates, and that is stable over years of thermal cycling is elusive. An ideal catalyst would lower the combustion temperature of soot from about 550 °C to at least 300-350 °C (typical of diesel exhaust). The combustion rate must be as great as the trapping rate to maintain constant pressure drop across the filter. Noble metal catalysts have potential, but they are becoming ever more expensive, making the costs prohibitive for larger engines. Complex mixed phase catalysts have shown promise for soot combustion, but the temperatures to maintain a constant pressure drop are too high (370 °C). Also, the best catalysts of this type are molten at the operating temperature, raising questions about migration of the active components and their long-term viability. [2,3]

Similar dilemmas exist for NOx reduction efforts in methane-burning gas turbine power plants. The homogeneous combustion of methane is efficient at high temperatures, but these temperatures lead to formation of NOx as a byproduct. Preventing NOx formation by catalytically lowering the temperature of combustion clearly has advantages over treating the exhaust stream to remove the NOx, but a number of issues have slowed commercial acceptance of this approach. The catalyst support is subjected to large temperature swings and gradients that tend to destroy the structural integrity of many ceramics. In addition, the catalysts need to initiate methane combustion at temperatures of 400-500 °C, but be thermally stable to temperatures of 1400 °C. [4] Supports more durable than the standard cordierite [5] and catalysts more thermally stable than the typical platinum [6] must be developed for application to this problem.

Drawing on our expertise in ceramic fabrication, catalyst design and characterization, combustion and oxidation chemistry, and exhaust characterization and treatment, we propose to

develop novel and unique ceramic catalytic combustors, and self-regenerating particulate traps that exhibit a revolutionary improvement in performance over commercially available systems - all in a simplified package.

1.2 Technical Issues

Of the five criteria listed above for supports and/or traps, the most challenging combination to achieve is the fabrication of a structure with a high surface to volume ratio that maintains a high permeability and low pressure drop. Currently, most companies use Corning Inc's extruded cordierite (ceramic) "honeycomb" structures in an attempt to achieve this balance. Others use ceramic "foams." Examples of these structures are shown in Fig. 1. Despite the successful application of the cordierite honeycomb to automotive catalytic converters, both honeycombs and foams have some fundamental weaknesses that hinder their usefulness in harsh, high-velocity diesel filter and methane combustion environments.

- For filter applications, half the channels on each end of the honeycomb structures must be plugged so that gas entering the structure must permeate through pores in the walls to exit the opposite end of the structure. This creates higher pressure drops than are required for optimal performance. At the high flow rates of these applications, foam structures also have unacceptably high pressure drops.
- The ceramic foams are random structures that exhibit variable surface area and pressure drop part-to-part.
- Cordierite is a material that is optimal for extrusion of thin-walled structures but is very susceptible to high temperature corrosion. The melting temperature of cordierite is >1400 C however corrosion products with inorganic impurities can begin to form at temperatures as low as 600 C. [1]
- The strength and resistance to mechanical shock is low.

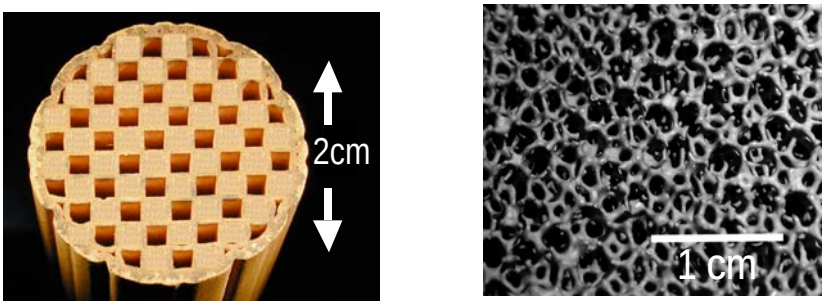


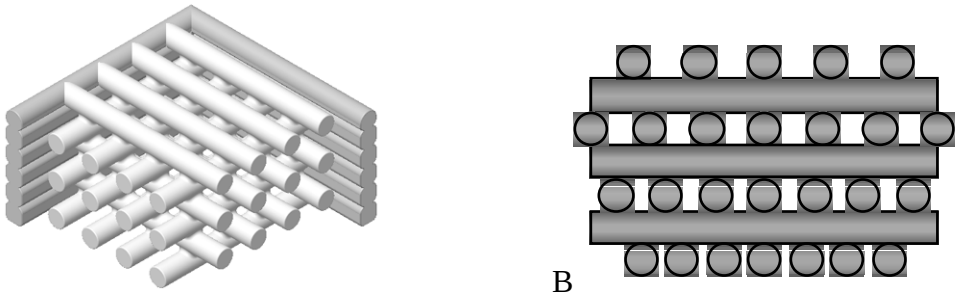
Figure 1: A) Cordierite honeycomb soot trap; B) Ceramic foam trap.

Even Corning Inc. is actively conducting research to find alternative materials and more permeable porous structures to make more reliable particulate traps. [7] However, even if the currently known R&D efforts are successful, they will only provide incremental advances. We propose a revolutionary approach utilizing a novel structure that will improve catalyst performance, strength, and high-temperature corrosion resistance.

1.3 Technical Approach

Inherently different from honeycomb extrudates or ceramic foams, our design is a three-dimensional crosshatched mesh that cannot be manufactured with traditional techniques. Our structures have layers of precisely spaced rods in alternating crosshatched patterns forming face

centered tetragonal stacks of rods (i.e., a “lattice"). See Fig. 2a. The fabrication method, termed robocasting, is a freeform layered manufacturing method developed at Sandia [8] and inherently ensures that the rods meld together and form a strong bond upon sintering. The sintered lattices have controlled porosity in three dimensions, but no line-of-sight pathways. This macrostructure provides tortuosity and a high surface to volume ratio while maintaining predictable permeability and low-pressure drop. The lattices may be improved further by incorporating graded porosity (as shown in Fig. 2b) and/or porous rods. These novel architectures are the basis of our supports and traps. Note that this fabrication technique is not only more versatile in terms of the shape of the ceramic product, but also allows a broader range of fabrication materials to be used.



A B

Figure 2: A) Schematic of a lattice structure showing that uniform pores are accessible in all directions. B) Cross-section of a lattice structure showing the potential for structures with graded pore sizes.

2. Support Structures for Enhanced Catalytic Activity

2.1 Introduction

Robocasting is a moldless fabrication technique developed at Sandia National Laboratories in [8-10] Early work demonstrated the usefulness of this process for the rapid prototyping of ceramics. Further development proved the utility of the process for metals, polymers, and composites in a variety of shapes, including self-supporting lattice structures.[11] These lattice structures are novel in their complexity and fabrication method and are being investigated for their use in such applications as photonics, [12,13] active ceramic composites,[14,15] and bone scaffolds.[16,17] This work will focus on the recent application of these structures as catalyst supports. In the robocasting process, highly concentrated suspensions containing ceramic powder and solvent (water) are deposited, or “written”, in a layer-wise fashion. The process is conceptually similar to icing a cake, with twodimensional layers of “icing” being sequentially deposited, ultimately forming a three-dimensional object. Controlling the viscous behavior of the ceramic suspension to a paste-like consistency enables shape retention of the deposited lines, or rods, of material until drying has taken place. Proper adjustment of the ceramic suspension viscosity allows for the creation of selfsupporting lattices whose structure is conceptually similar to that of precisely stacked “Lincoln Logs”. The placement of these rods can be tailored to obtain either straight-through pathways or more tortuous pathways, depending on design requirements. This study focuses on a face-centered-cubic type of structure as seen in Figure 3, in which there are no line of sight pathways in the direction of gas flow. It was thought that these porous structures could enhance mass-transfer rates above those found in traditional straight-channel extruded-honeycomb monoliths with a minimum penalty in pressure drop.

Flow Direction

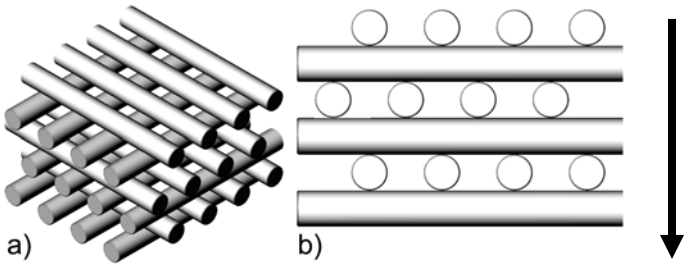


Figure 3: Schematic of FCC lattice structure: a) isometric and b) side views.

Although these structures might be applicable to a wide range of catalyst applications where monoliths are currently used, this initial work explored their utility for the catalytic combustion of methane for low-NOx power generation applications. This is a very demanding application that requires catalysts that remain active at high temperatures (up to 1300 °C) and high flows. Upstream velocities in gas-turbine power generation units can exceed 30 m/s. To accommodate these high flow requirements, monolithic supports with little resistance to gas flow are a necessity, and traditional extruded-honeycomb-type monoliths are most commonly studied for this application. The narrow channels in these structures promote laminar flow. Therefore, mass transfer can become a limiting factor, provided that a suitably active catalyst can be identified. In these cases, turbulent flow through robocast lattice monoliths will promote higher mass-transfer coefficients, thus enhancing conversions. Further, chemical degradation and mechanical instability of cordierite (commonly used to fabricate catalyst monoliths) at 1300 °C suggests that other support materials might be more useful.

Because the goal was to evaluate the utility of the monolith, and not to develop a new catalyst, a ceramic hexaaluminate ($BaMn_2Al_{10}O_{19-}$) material[18-20] was chosen as the catalyst. Hexaaluminate catalysts have recently attracted much attention for the combustion of natural gas given that they resist sintering at high temperatures. The $BaMn_2Al_{10}O_{19-}$ formulation used here is reported to have one of the highest activities of the hexaaluminate catalysts studied.[21,22]

2.2 Experimental Procedure

The extruded honeycomb monoliths commonly studied for combustion applications have a two-dimensional cellular structure with 62 pores/cm^2 (400 pores/in^2) and a cell wall thickness of ~180 μm (0.007 in), which corresponds to a geometric surface area of 27cm^2/cm^3 (69 in^2/in^3).[23,24] Porous cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) is typically used to fabricate the monoliths due to its moderate strength (20-90 MPa), high thermal stability, resistance to chemical corrosion, and cost effectiveness. Samples of cordierite honeycomb monoliths (Johnson Matthey, London, UK) were cut to 12.7 mm in thickness and approximately 22 mm diameter to fit in a quartz reactor tube. These samples had 177 pore channels, corresponding to a total geometric surface area of 167 cm^2 and an open porosity of 77%. Similar samples were prepared from an γ-Al_2O_3 washcoated (30 weight %) cordierite monolith. The γ-Al_2O_3 washcoat was found necessary to prevent reaction of the hexaaluminate catalyst with the cordierite (see below).

Robocast monoliths of similar dimensions (12.7 mm by 22 mm) were prepared from high purity (99.8% Al_2O_3) alumina (Alcoa A15, Alcoa World Chemicals, Leetsdale, PA) and sintered to >99% density at 1650 °C for high strengths (275 MPa). In addition, robocast lattice monoliths composed entirely of the ceramic $BaMn_2Al_{10}O_{19-\alpha}$ catalyst were also fabricated. A range of

geometric surface-area-to-volume ratios is obtainable (15-43 cm^2/cm^3) for the robocast lattices by altering both rod size and spacing. In this case, the geometric surface area of the robocast lattices were matched to the cordierite with the help of a CAD software package, SolidWorks (SolidWorks Corporation, Concord, MA). Using this software, surface areas were calculated for CAD models with various rod sizes and spacings until a matching surface area of 167 cm^2 was obtained. Several combinations of rod size and spacing matched this target surface area, so a computational-fluid-dynamics software package, FloWorks (Nika GmbH, Frankfurt, Germany), was used to determine a rod size-and-spacing combination that provided the most turbulence without dramatically increasing pressure drop. The flexibility of the robocasting process enabled a replica of the CAD model to then be fabricated. The final robocast lattice samples exhibit 45% open porosity with no line-of-sight pathways, with rod diameters of 725 μm, and rod spacings of 500 μm.

The BaMn-hexaaluminate catalyst was synthesized by co-precipitation of Ba, Mn, and Al salts.[25] Calcination to 1300 °C yielded catalyst powder with a surface area of 12 m^2/g. An aqueous slurry containing 15 vol% catalyst powder was dispersed with an ammonium salt of polyacrylic acid (Darvan 821A, R.T. Vanderbilt Co. Inc, Norwalk, CT) in aqueous solution for washcoating onto the ceramic monoliths. The washcoats were applied by filling the sample with slurry and removing excess material with forced air. The procedure was repeated until the desired catalyst loading was obtained. It was determined that calcination to 1300 °C after washcoating and drying was required to produce a relatively strong catalyst-to-support bond for the robocast-alumina samples. Bonding of the catalyst onto the alumina support was poor at lower calcination temperatures, and testing could not be reliably performed. At temperatures greater than 1400 °C, visible changes could be seen in the substrate that suggested the catalyst was reacting with the alumina substrate. The washcoated cordierite and alumina/cordierite honeycombs were also calcined to 1300 °C to provide a good bond between catalyst and substrate and for consistency since the calcination had the potential to reduce the surface area of the hexaaluminate catalyst.

The effects of calcining the hexaaluminate in contact with alumina and cordierite substrates were probed by preparing mixtures (2:1 by weight) of alumina or cordierite powder (prepared by grinding a monolith) with the hexaaluminate powder. Portions of these mixtures were subjected to calcination at 1300 °C. The catalytic activities of the as-prepared and calcined mixtures were then compared to a sample of the as-prepared hexaaluminate. Since mass transfer in the powder samples would be similar in all cases, any differences were attributed to solid-state interactions between the catalyst and substrate powders.

For the monoliths, reaction testing was performed in a tube furnace fitted with a 22 mm ID quartz tube. The catalyst monoliths were held in place with a thin layer of quartz wool wrapped around the exterior of the monoliths. This arrangement also served to prevent flow from bypassing the monolith. Reactive gases (10% O_2, 2.5% CH_4, balance N_2) were flowed over the monolith at 205 sccm (standard cubic centimeters per minute). Higher flow rates, which are closer to those used in methane power generators, are currently being investigated with favorable preliminary results. The temperature was measured by thermocouples placed at the interior of the quartz wall adjacent to the monolith and touching the upstream end of the monolith inside of the reactor. Effluent gas concentrations were quantified with an online gas chromatograph utilizing molecular sieve (CH_4, CO, O_2) and Poraplot Q (CO_2) columns. The effluent was conditioned by passing it through a condenser to remove excess water prior to introduction into the GC. With this arrangement material balances typically were greater than 95%. In all cases, virtually no CO is formed over the hexaaluminate catalyst. Methane conversion data was collected at temperatures ranging from 400-800 °C, typically in 25 or 50 °C increments. After reaching

temperature, steady state was quickly established and verified by collecting a series of at least 7 data points at each test condition.

Testing of the powders was done in a similar fashion to monolith testing, using a 5 mm I.D. quartz reactor tube, a total flow rate of 55 sccm, and 0.05 g of hexaaluminate powder (either pure or present in a mixture with powder support material). Powder samples were dispersed in a matrix of quartz sand to minimize local heating effects from the exothermic combustion reaction. Thermocouple readings verified isothermal operation. According to well-established interphase transport criteria, the experimental conditions detailed above for powder samples were sufficient to eliminate any bulk mass transfer effects during activity testing.[26] Additionally, only X-T data at low conversions (<10%) was utilized during the kinetic analysis to satisfy the assumption of differential operation. The calculated kinetic parameters from the powder data were used to simulate an X-T plot for methane conversion over the monolithic samples, with appropriate corrections for catalyst loading and space velocity. It was assumed that pore diffusion would be similar for both the $BaMn_2Al_{10}O_{19-}$ powder and washcoat, and so this effect, if present, was assumed to be part of the kinetic expression.

2.3 Results and Discussion

Two of the hexaaluminate-coated monoliths used in catalyst testing can be seen in Figure 4. Although these monoliths have different internal structures, the geometric surface areas coated with catalyst and exposed to the gas stream are identical at 167 cm^2 with overall dimensions of 22mm OD, and 12.7mm height. Figure 5 compares the results for a robocast lattice and extruded honeycombs (with and without alumina washcoats) nominally loaded with about 0.35 g of hexaaluminate. No visible degradation of the robocast or cordierite support was noticed over the temperature range tested. Also shown in Figure 5 are the results for a control experiment carried out with no catalyst present. At the relatively slow flows tested, 100% methane conversion is achievable at 800 °C due to homogeneous reactions. Figure 5 shows that the robocast lattice exhibited higher conversions than the honeycombs at all temperatures greater than 450 °C. Methane conversion at 600 °C is approximately six times greater for the robocast lattice as compared to the extruded honeycombs. This is despite the fact that the actual residence time in the robocast lattice must be ~58% of that in the honeycombs (recall the bulk porosity of robocast lattice is 45% compared to 77% for the honeycomb).

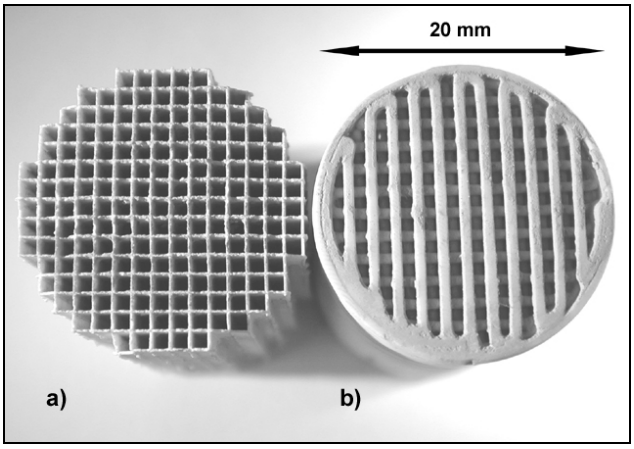


Figure 4: Monoliths of similar outer dimensions and surface areas coated with BaMn-hexaaluminate; a) extruded honeycomb and b) robocast FCC lattice.

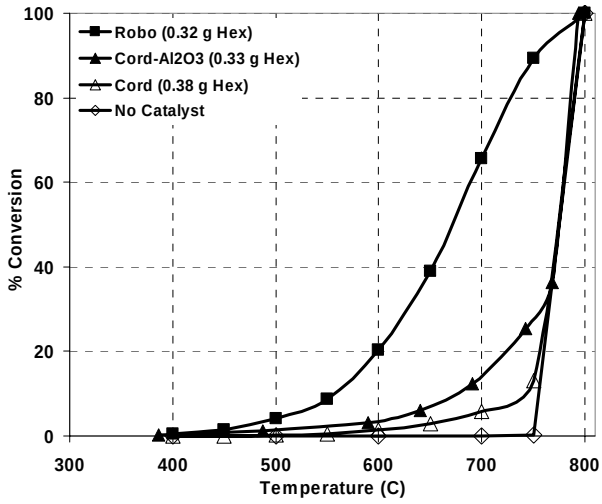


Figure 5: Methane conversion comparison of robocast and honeycomb-supported hexaaluminate catalyst systems.

Figure 5 also shows that the alumina coated cordierite monolith outperforms the non alumina-coated honeycomb, despite the fact that, due to variability in the washcoating procedure, the non alumina-coated sample was loaded with about 15% more catalyst. The reason for this unexpected behavior can be found in Figure 6, which shows the results for the powder/support mixtures. The as-mixed powders did not show any appreciable deviation in conversion from the pure hexaaluminate catalyst. The calcined alumina/catalyst mixture also behaved similarly to the pure hexaaluminate. However, the sample of cordierite and hexaaluminate powders calcined together at 1300 °C showed a significant loss of activity, indicating a deleterious reaction between the catalyst and the silica-rich cordierite. The alumina washcoat therefore acted as a barrier layer between the catalyst and cordierite substrate, preventing or limiting reaction between the two materials. Alumina barrier layers have been previously used to prevent reaction between hexaaluminates and aluminum titanate substrates.[19]

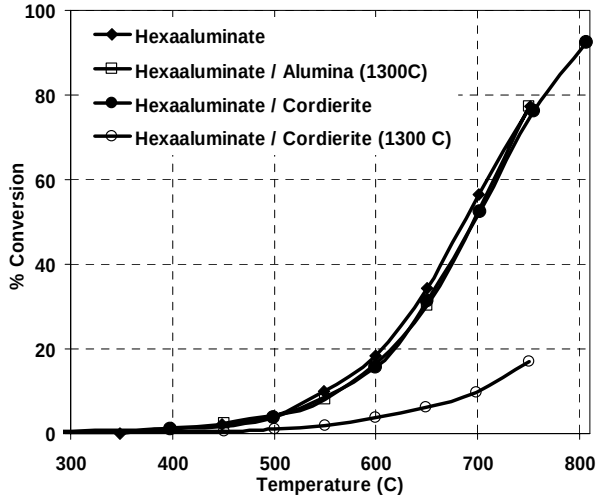


Figure 6: Methane conversion comparison for intimately mixed catalyst and substrate materials.

Additional studies were carried out to determine the optimal loading of hexaaluminate on the robocast monoliths. These studies compared the flow behavior (pressure drop) and relative activities for several catalyst loadings on identical robocast supports. The optimal loading was found to be about 0.9 g of catalyst on the chosen monolith geometry or about 5 mg/cm^2 of geometric surface area. At higher loadings, pores began to clog to the extent that pressure drops across the monolith began to significantly increase. Further, only incremental improvements in overall methane conversion were realized with higher loadings. Kinetic parameters derived from the powder data and assuming a first order reaction were used to show that at loadings up to about 0.9 g, the washcoated robocast monoliths performed like powders. That is, there were no mass transfer limitations within the bulk or catalyst washcoat layer at the conditions tested here.

The optimally coated robocast lattice is compared to a lattice with 1/3 the optimal loading, and a lattice constructed entirely out of hexaaluminate in Figure 7. At 600°C, the pure catalyst monolith exhibits a conversion twice that of the optimally washcoated lattice. Further, 100% methane conversion is achieved at 700°C, which is 100°C less than all other samples tested. The pure catalyst monolith also has reduced light-off temperature. An investigation is currently underway to determine the mechanism for this temperature reduction. We note, however, that fabricating the monolith out of the hexaaluminate allows us to place a larger amount of catalyst in the reactor without encountering problems such as flow restrictions that would counteract the higher loadings. In addition, we note that fabricating the monolith out of the catalyst inherently leads to a uniform distribution of the catalyst. There are also potential differences in surface roughness or porosity that may be contributing factors. In any case it is clear that direct fabrication of a monolith from the catalyst is advantageous, particularly since the catalyst is easily produced from relatively inexpensive components and can be easily adapted to the robocasting process.

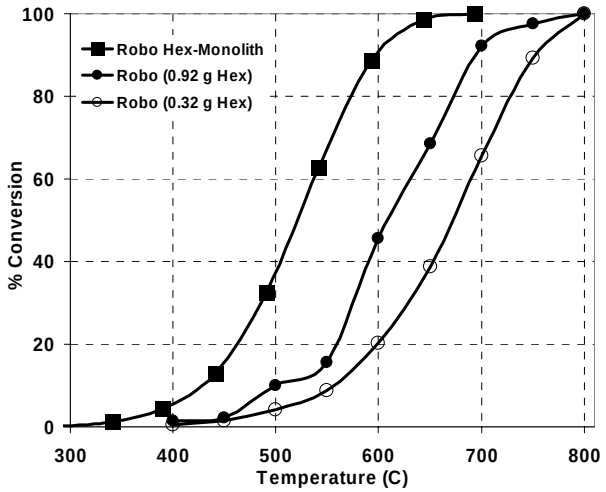


Figure 7: Comparison of pure-catalyst and catalyst-supported robocast lattice structures.

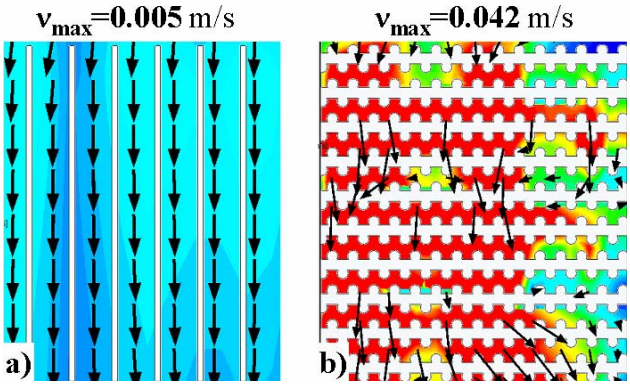


Figure 8: Cross-sectional views of flow velocities for a) extruded honeycomb and b) robocast lattice supports.

Flow velocities calculated with FloWorks along a cross-section of the diameter is shown in Figure 8 for the two different monolith geometries. Red areas indicate regions of high flow velocity; blue regions are low flow velocities with arrows indicating local flow directions. FloWorks allows many fluid and solid parameters to be adjusted for modeling. For this study, volumetric flow rates, exit pressures, and gas properties (such as density and viscosity) were matched to actual experimental parameters. Modeled extruded-honeycomb structures exhibited pressure drops of 6.9 Pa (0.001 psi) and a distribution of flow velocities ranging from 0.0 to 0.005 m/s (0.0 - 0.016 ft/s). Modeled robocast-lattice structures exhibited pressure drops of 207 Pa (0.030 psi) and a distribution of flow velocities ranging from 0.0 to 0.042 m/s (0.0 - 0.138 ft/s). Even though the pressure drop across the robocast lattice was 30 times greater than the extruded honeycomb, this is still a relatively low pressure drop. We also designed alternate robocast structures with reduced pressure drops more in line with those of extruded monoliths. These structures still exhibit improvements in catalytic performance and are reported in previous SAND Report [27]. The greater distribution of flow velocities exhibited in the robocast lattices indicate that the internal structure is creating turbulence that should promote mass transfer to the catalyst surface. Laminar flow is seen in the extruded honeycomb.

These results of the flow modeling are consistent with the data obtained for the actual monoliths. No mass transfer limitations were observed for the robocast monoliths, and the robocast lattice gave greater conversions than the honeycomb monoliths. It is possible, however, that even in the case of the honeycomb with the protective alumina washcoat, that part or all of the difference could be attributable to interactions between the catalyst and the underlying cordierite. For clarification, additional tests were completed to quantify the mass transfer coefficients and pressure drop behavior under a variety of flow conditions.[27] The results are reported in a SAND report and conclusively show that the robocast lattices improve mass transfer coefficients.

2.4 Conclusions

A low cost ceramic catalyst, BaMn-hexaaluminate, was washcoated onto traditional extruded honeycomb and robocast lattice support structures. The complex internal structure of robocast lattices promotes turbulence, which enhances mass transfer of reactants to the catalyst surface over that in monoliths with straight-through channels. This could have important benefits for a number of environmental applications that require highly active and/or costly catalysts, e.g. noble metals. At the relatively low flow rates used here, the pressure drop penalty for the increase in mass transfer is insignificant.

The robust capabilities of the robocasting process allowed tailoring of the lattice geometries to match overall dimensions and surface areas of extruded honeycomb samples. These capabilities permitted a more direct comparison of the effect of support macrostructure on methane conversion. In addition, the robocasting process allowed a monolith to be easily and directly fabricated from the catalyst material itself. With equal amounts of catalyst, robocast lattices converted approximately six times more methane at 600 °C than extruded honeycomb supports. Maximizing the catalyst loading on robocast monoliths further increased conversion by a factor of two, converting 45% of the methane at 600 °C. A pure hexaaluminate robocast lattice monolith further increased conversion another factor of two converting 89% of the methane at 600 °C, and 100% of the methane at 700 °C.

2.5 Other Applications

In FY04 we completed similar studies to those described above for catalysts and supports for two potentially important reactions. Iron / potassium catalysts were developed, applied to our lattices, and used to demonstrate their effectiveness for the dehydrogenation of butene. This important reaction is used to produce synthetic rubber. This reaction is exothermic and can be problematic because “hot spots” can develop within the reactor. Our lattice supports demonstrated the ability to dissipate heat quickly to maintain temperature uniformity throughout the reactor. We also developed lattice supports with nickel-hexaaluminate and demonstrated their utility in the extremely important “syngas” reaction that produces carbon monoxide and hydrogen from methane. These byproducts are used for everything from diesel fuel to plastics. Current approaches to the production of syngas use noble metal or nickel containing catalyst. These materials deactivate at high temperatures and over time and have a tendency to form reaction-inhibiting coke. Our nickel-hexaaluminate lattices proved to inhibit the formation of coke and remain stable even at temperatures greater than 800 C.

3. Diesel Particulate Traps

Our goal was to develop materials and methods for trapping soot from an exhaust stream with a lattice structure that also was catalytically active on its surface. The idea is to catalytically combust the soot into carbon dioxide and water just as soon as the lattice traps the soot particles. In principle, there would be no need to replace the trap because it would be self-cleaning. Part 1 of this endeavor was to fabricate lattice structures that could be used to trap soot particles from a diesel engine exhaust stream. Part 2 was to develop strategies and materials that can combust the trapped soot particles and regenerate the trap.

3.1 Trapping

Traps were fabricated by robocasting alumina into lattices structures with rods that were 1.5 mm in diameter. A sample with an overall diameter of 78 mm and 26 mm thick was attached to the exhaust from a 1965 Mercedes diesel engine. Over a five-minute period the lattice was able to trap 27% of the soot. The dirty trap is shown in figure 9. Considering the small cross-sectional area and thickness of this trap, a collection efficiency of 27% is very encouraging. In another diagnostic test, alumina lattices were placed in a stream of soot particles generated with a torch and the concentration and size distribution of the soot particles that passed through the trap were measured with a laser technique. The results are shown in figure 10 and seem to suggest that the lattice can trap some soot particles smaller than 100 nm. However, it must be clearly stated that

this is a preliminary result and it has not been reproduced. It is speculated that the presence of the lattice may alter the concentration of the soot particles produced upstream thereby giving an erroneous result for the concentrations measured downstream. More controlled experiments must be completed to verify this result.

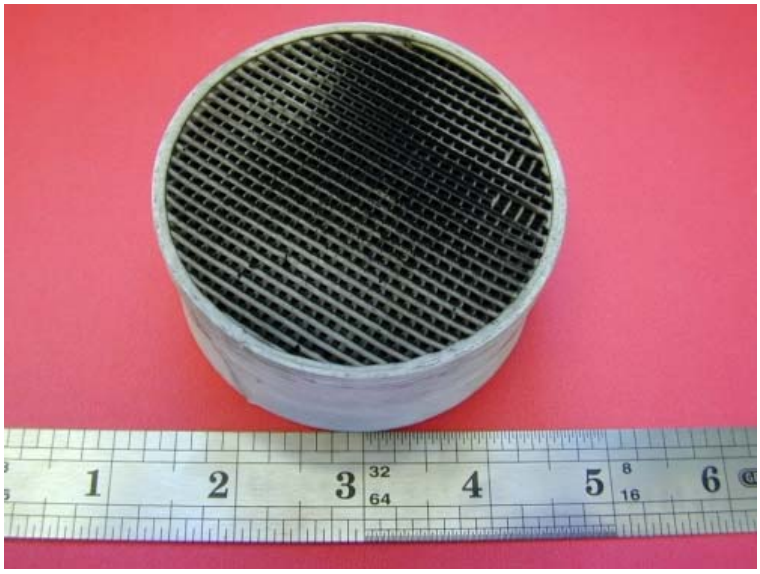


Figure 9: A 26 mm thick alumina latticed is shown with soot trapped on its surface after being placed in the exhaust stream of a 1965 Mercedes diesel engine.

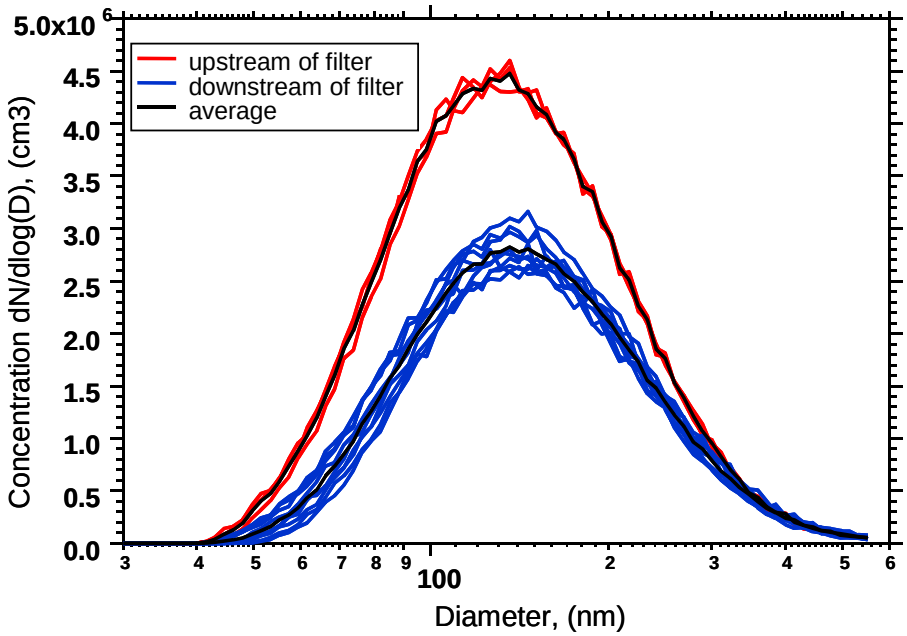


Figure 10: Preliminary (unconfirmed) data showing the concentration and size of soot particles before and after an one inch thick alumina lattice.

3.2 Trap Regeneration

There are two different strategies for the in-situ regeneration of our traps(a catalyst capable of combusting soot at low temperatures and/or an electrically resistive lattice that can be heated to induce soot combustion. If successful, either one of the strategies may be satisfactory or both strategies may be combined into a single package and implemented together.

The first approach requires the development of a catalyst that can combust soot at temperatures significantly less than 400 C (i.e., the temperature of diesel exhaust). A cesium-vanadate material was developed and may be useful; however, the presence of vanadium in exhaust streams may not be environmentally desirable. Therefore, an alternative cesium / copper / molybdenum material was developed and shown to combust soot at 330 C in a preliminary test performed in an oven. A test in a diesel exhaust stream has not yet been completed.

In parallel with the work discussed above, we developed materials and processes for fabricating lattice traps that are electrically resistive. Both silicon carbide and zirconia / metal composites lattices were successfully developed and electrically heated to temperatures as high as 800 C without any noticeable oxidation or corrosion. The electrically resistive traps were observed to combust soot when their temperature reached 600 C. Approximately 100 watts of power was required to reach 600 C and regenerate the trap. A red-hot SiC lattice is shown in figure 11.

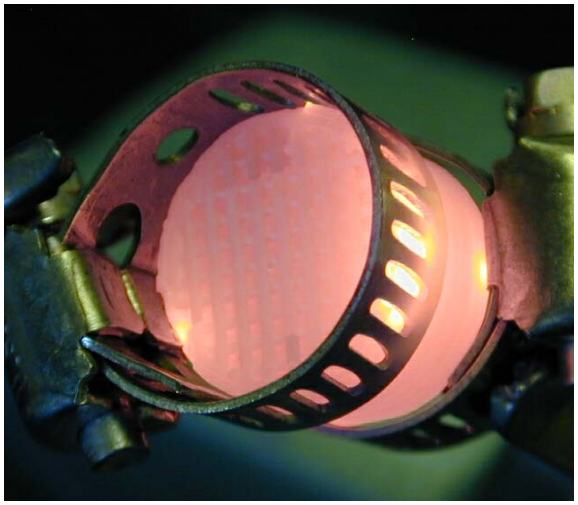


Figure 11: A SiC lattice made into a resistively heated trap that glows red-hot to assist in the combustion of trapped soot particles.

3.3 Conclusions

Our goal was to create a prototype diesel particulate trap that is capable of in-situ regeneration. While an actual prototype was not fabricated, all of the individual components necessary for a completed prototype were demonstrated. A 26 mm thick lattice structure was capable of capturing 27% of the soot produced. Lattices were developed with electrical resistivity such that they could be heated to high temperature and induce the combustion of trapped soot. Catalysts were developed which demonstrate the ability to combust soot at temperatures less than 400 C. The next step is to apply the appropriate catalyst to our electrically heated lattices, assemble the device into a prototype package, and test the prototype on diesel engine with diagnostics for capture efficiency and pressure drop. This test remains to be completed.

The ultimate goal is to create a trap that captures >90% of the soot. Thicker lattices with more cross-sectional area may or may not be able to reach that goal. However, even if that goal is not met, lattice traps may still be useful as pre-filters that will extend the lifetime of more conventional honeycomb wall filters.

4. Hydroxyapatite Lattices for Bone Scaffolding: A Case Study

4.1 Summary

The Mandible Reconstruction Project is a unique, ongoing, multi-disciplinary effort involving the University of Illinois' College of Engineering, the Beckman Institute for Advanced Science and Technology, Sandia National Laboratories, and Carle Foundation Hospital to develop an alternative approach to bone replacement--one that obviates the bone harvest surgery without diminishing the superior clinical outcomes associated with autografting. A case study was completed that demonstrated the feasibility of creating customized bone implants in a real clinical setting. An integrated workflow was created among the collaborators to progress from surgeon to modeler to fabrication of a perfectly-fitting custom device.

4.2 Background

The replacement of bone lost through disease or injury presents a continuing clinical challenge. The current "gold standard" is autograft bone, i.e. bone taken from another site in the body. The surgical procedures for the harvesting of such bone can result in complications that are "minor" (hematoma, temporary sensory loss, acute pain); or "major" (permanent sensory loss, chronic pain, infection). Complication rates exceeding 30% have been reported for autograft harvesting from the iliac crest of the pelvis, a common source for autograft bone. The alternative to autografting is implantation of cadaver bone. From a clinical perspective this is an even less attractive option which increases the complication rates associated with autografting and adds the risk of disease transmission to the procedure.

4.3 The Process

Using the case of a 73 year old female who has experienced severe bilateral bone loss in the mandible, materials scientists, engineers, medical 3D artists, computer-aided designers, and the patient's attending physician created a workflow by which a synthetic ceramic scaffold was designed, and fabricated specifically for this patient. This workflow involved true collaboration between all parties involved, as the surgeon sought to transfer his intuitive knowledge of the precise structure of the implant to the 3D modelers at Beckman, who then in turn transferred a CAD model of the implant to Sandia for fabrication.

As shown in Fig. 12, the CT scan provides information about the shape and density of the bone that is present in the patient's damaged mandible. However, the implant has to fit into the region where no bone (or CT data exists). Therefore imaging technologists worked with the surgeon to define the boundaries for the implant and made accommodations for an existing nerve (see Fig. 13).

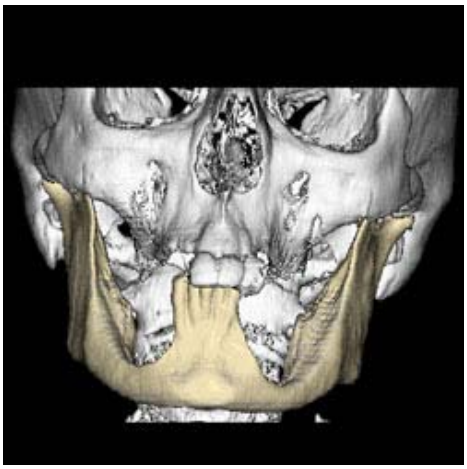


Figure 12: A volumetric three-dimensional reconstruction made from a CT scan shows the patient's damaged mandible.

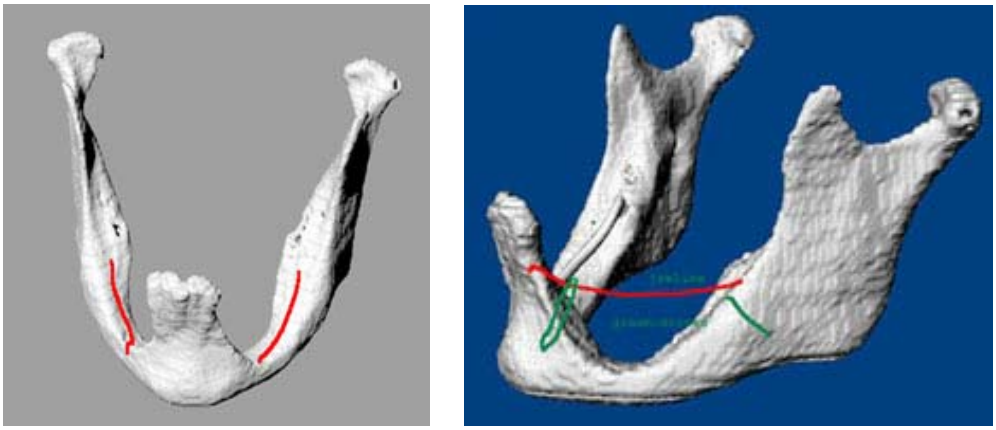


Figure 13: Sketches by Sinn-Hanlon and Goldwasser defining the path of the inferior alveolar nerve (left) and the boundaries of the implant (right).

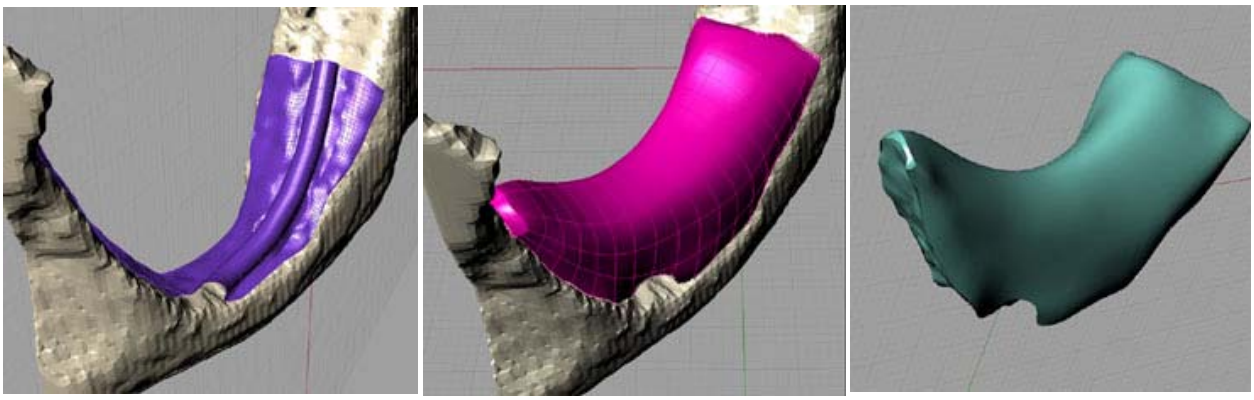


Figure 14: The final precise-fit undersurface of the implant with nerve accommodating canal (left), the final model blended onto the surface of the damaged mandible (center), and an isolated view of the final CAD model showing the desired shape of the implant (right).

Imaging technologists then created a computer-generated 3D model whose bottom surface precisely fit the eroded mandibular surface that it would rest on (see Fig. 14). A canal was built into the ventral surface of the implant that was large enough to accommodate the exposed nerve,

but would leave an adequate amount of contiguous surface on either side for jaw strength. The top surface of the implant was designed with the intent of restoring the natural shape of the jaw and providing a surface that would support dentures. The two surfaces were welded together to complete the model for the implant.

The 3D computer model was then e-mailed to Sandia, where the implant was fabricated. The computer model of the implant contained the information for the external surfaces and overall shape of the implant. However, in order to be an effective scaffold material the implant needs to have an ordered porous macrostructure within which natural bone can grow. The desired porous macrostructure looks like an assemblage of rods in the form of a three-dimensional lattice. Sandia's patented freeform fabrication process called 'robocasting' was used to make blocks of the porous lattice scaffolds. For this project, the scaffold material is hydroxyapatite, a substance chemically identical to the mineral component of human bone. These scaffold structures can be made strong enough to withstand the forces that natural bones are exposed to and are therefore potentially useful as load-bearing implants. A robocasted scaffold is shown in Fig. 15. To make the scaffold into the shape of a customized implant, like that shown in Fig. 14, an oversized block of scaffold material was machined with a CNC mill. The implant designed to fit into the damaged mandible is shown in Fig. 16. The porous structure of the scaffold will promote the growth of new bone into the structure. Over a period of several months new bone will continue to grow as the scaffold material is simultaneously resorbed. Eventually, the entire damaged region will be occupied by natural living bone.

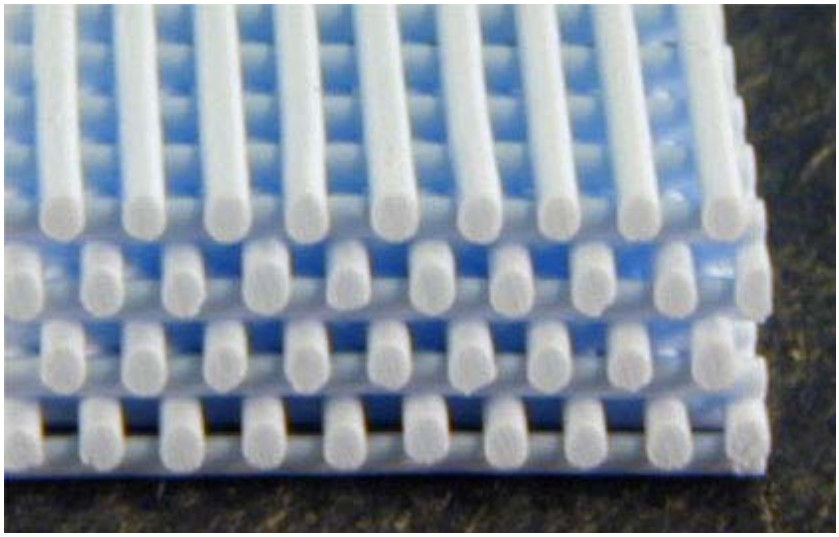


Figure 15: An example of a hydroxyapatite scaffold is shown here. The diameter of each rod in this image is approximately 300 microns.

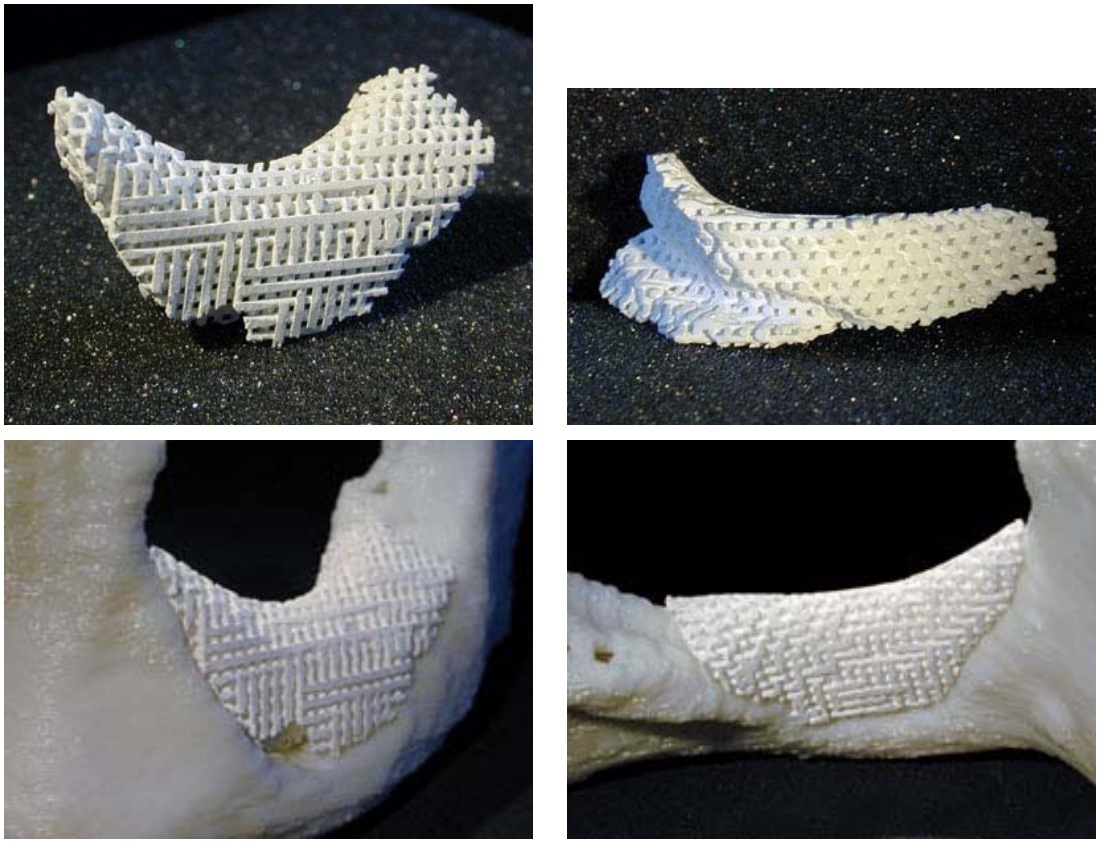


Figure 16: Various views of a porous scaffold designed to be implanted into a damaged mandible. Bottom images show the implant placed in a plastic replica of a damaged mandible.

Finally, during the patients' previously scheduled autograft procedure, the implant was sterilized in an autoclave and inserted into place for fit testing (see Fig. 17). The surgeon proclaimed the implant to 'fit like a glove'. Unfortunately, until FDA approval is obtained, an implant of this type can not be left in a human body and it was removed. A good deal of research remains to be done before these devices will be available for clinical use. While the initial findings have been encouraging, the rigorous process of establishing the safety and efficacy of this device will require a number of years of laboratory and clinical research and substantial investment. The ultimate goal is to develop a design approach that provides to the surgeon customized synthetic bone scaffolds that rival the healing and remodeling results now achieved with autografting. And one that provides to the patient safe and rapid healing without the risk and discomfort of the additional surgery that autografting requires.

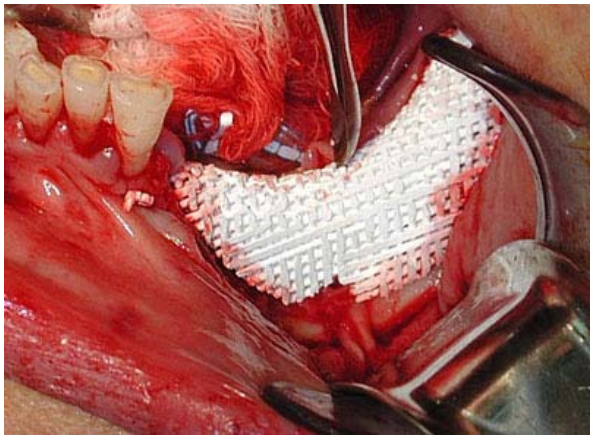


Figure 17: The customized robocasted lattice implant test-fitted in the patient’s jaw.

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